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Superconducting critical fields in niobium and niobium containing oxygen*

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In situ resistive measurements of the ratio of surface to bulk critical fields in thoroughly degassed pure niobium foils are found to agree well with theory over the temperature range $0.69 \leq t \leq 0.99$. This result is unchanged after reheating the samples above 2000 K, in oxygen atmospheres of up to 0.96×10^{-7} Torr. We have also observed a considerable increase in H_{c3} and H_{c2} in samples reheated at above 0.96×10^{-7} Torr, with the Ginzburg-Landau parameter κ rising to 3.04 after reheating at 5.0×10^{-7} Torr. Nonetheless, the ratio of critical fields remains 1.7 to $t = 0.97$. The increased critical fields can be attributed to increased surface roughness and faceting which occurs on heating in oxygen, resulting in a considerably diminished mean free path. An enhancement of H_{c3} above the value $1.7 H_{c2}$ was observed above $t = 0.97$ in these samples. The cause of this behavior has yet to be understood, although we suggest the presence of carbides at the surface as an explanation.

I. INTRODUCTION

The results of observations of sheath superconductivity in niobium have tended to deviate considerably from what are otherwise quite well supported theories. In particular, measurements of the ratio of surface to bulk critical fields (H_{c3}/H_{c2}) in this material by Hopkins and Finnemore,[1] and Ostenson and Finnemore,[2] have shown a pronounced decrease with increasing temperature near T_c, approaching 1.00 as a limit. This is in sharp disagreement with the St. James–de Gennes[3] prediction of a temperature-independent value of 1.7 in the local regime, and with nonlocal theory[4] which predicts a slow decrease to this limit as T_c is approached. Furthermore, and in contrast, measurements by Indovina *et al.*[5] show H_{c3}/H_{c2} to rise well above 1.7, appearing to diverge at T_c.

The explanation of these discrepancies which has gained the widest support is based on the observation that the theoretical approaches have assumed the composition of the surface to be identical to that of the bulk, and that the surface boundary can be treated as an ideal superconductor-vacuum interface. Such an assumption, while apparently satisfactory for many materials, may not be appropriate for real samples of niobium. Residual impurities, absorbed gases, grain boundaries, and other defects, might tend to give the surface region a nonideal quality which would indicate that caution should be used in applying the results of Refs. 3 and 4 to such a sample. The situation could be viewed as one in which the superconducting interaction strength has been altered near the surface, either depressed or enhanced, while the theory has assumed it to be uniform throughout.

What one would expect to measure as the ratio H_{c3}/H_{c2} in such nonideal samples has been given in theories by Hu,[6] and by Fink and Joiner.[7] The former starts directly from the microscopic theory and considers the effect of a layer of variable thickness and altered interaction strength on an otherwise homogeneous bulk. The latter generalizes the St. James–de Gennes approach, and includes the effect of a surface layer through an appropriate modification of the Ginzburg-Landau boundary condition on the order parameter near the surface. Both approaches agree in predicting a depression of the ratio H_{c3}/H_{c2} below 1.7, approaching 1.0 as a limit near T_c in the case where there exists a surface layer of depressed interaction strength. Likewise, both theories agree in predicting a rise above 1.7, with the ratio diverging as $(1-t)^{-1/2}$, in the presence of a layer with enhanced interaction strength at the surface. Good intuitive arguments to explain such behavior are presented in Ref. 6.

Such arguments appear quite compelling when compared with observations on niobium, and represent good progress in understanding sheath superconductivity in this material. The problem, however, has certain aspects which demand further work. For one, the precise nature of the surface layer resulting in the atypical interaction strength is not yet understood, nor is the related question of why quite different behavior has been observed by different investigators. Also, the question as to under what conditions it is possible to prepare a niobium sample which gives results consistent with the theories in Refs. 3 and 4, remains unsettled. Webb[8] has demonstrated that this is possible in very pure, single crystals of niobium. This knowledge would be important in applications to superconducting devices such as transmission lines, accelerators, etc. The present work was undertaken with the intention of providing insight into these questions. We have endeavored to form niobium samples with good surfaces through ultrahigh-vacuum high-temperature degassing, and to follow this with *in situ* measurements of H_{c3} and H_{c2} by recording resistive transitions in a magnetic field. In order to search for the origins of any de-

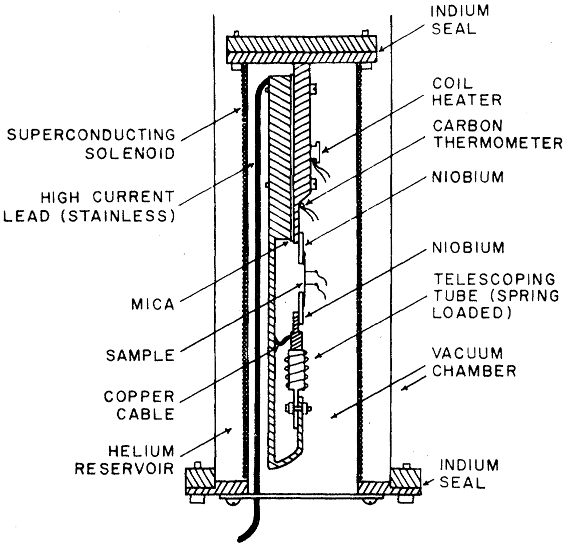

FIG. 1. Sample chamber.

partures from theory, we have reheated the same samples in increasingly higher pressures of oxygen and then remeasured the critical fields. The motivation for this is that much evidence has accumulated, indicating that it is quite difficult, if not impossible, to completely remove oxygen from the surface of a niobium sample, even with the most careful preparation techniques.[9] This is primarily a result of the high diffusion rate and low evaporation rate for oxygen in niobium in the temperature range 800–1900 °C. Since NbO, the compound which remains, has the relatively low T_c of about 1.3 K, its presence might be an explanation of the data in Refs. 1 and 2. Briefly, we have found that our preparation techniques do yield good agreement with theory for degassed niobium, including the region near T_c. We have also found that introducing oxygen does not tend to depress H_{c3}/H_{c2}, in disagreement with the interpretation given above, but does lead to a set of other interesting effects which we present.

II. EXPERIMENTAL DETAILS

Our samples were prepared from Marz grade 0.05-mm niobium foil obtained from Materials Research Corp. The supplier lists tantalum, at 300 ppm, as the major impurity, along with 23-ppm oxygen, 8-ppm carbon, and other elements in trace amounts. The starting material had a residual resistance ratio of about 70 and presented a dull metallic luster. A strip roughly 1 mm wide by 25 mm long was cut from the foil, along with two additional strips each approximately 13 mm long. The former was to serve as our sample while the latter were to be attached as voltage leads for a four-terminal resistance measurement. The strips were lightly etched in a 50-50 mixture of HNO_3 and HF, thoroughly washed and dried. The voltage leads were spot welded at right angles to the sample at points 3 mm from its center, leaving a rectangular cylinder $6\times0.05\times1$ mm between the voltage leads, on which measurements were to be taken. Figure 1 shows the design of the sample chamber in our cryostat. The vacuum could be maintained at 1.6×10^{-9} Torr under the action of ion pumping, a titanium sublimation pump, and cryogenic pumping by the liquid-nitrogen-cooled surfaces of the cryostat. In addition, oxygen could be introduced in a controlled way through a bleeder valve. For these runs, the titanium sublimation pump was not used. The superconducting solenoid had a calculated field-current coefficient of 273.5 G/A, and was swept by a programmed power supply.

Cleaning of the samples was accomplished in the ultrahigh-vacuum environment by passing approximately 10 A through it. This resistively heated the the foil to above 2000 K. Sample temperature during the heating process was determined by monitoring its resistance ratio $R(T)/R(300\,\mathrm{K})$. This function was linear, and had been determined with the aid of an optical pyrometer during a calibration run using another foil cut from the same starting material.

The portions of the sample holder in immediate contact with the sample were made of 0.25-mm-thick niobium strips to prevent contamination at the points of contact. The attachment was made by spot welding. The other ends of the niobium strips were spot welded to the rest of the holder. One end of the sample holder had a spring-loaded movable portion which kept the sample under slight tension and prevented permanent warping during the heating stage. During heating, the helium reservoir was filled with liquid nitrogen. As a result, the surfaces of the sample chamber were maintained at or near liquid-nitrogen temperature. A carbon resistor located 1 in. from the sample did not rise above room temperature. Thus outgassing of the sample chamber was not a problem even at the very high sample temperatures reached. Initial degassing was maintained for about 10 h. Calculation of degassing times to reach 0.001-at.% bulk oxygen concentration for a 0.05-mm-thick sample from the work of Strongin *et al.*[9] gave a result of 5 h. We observed no significant change in low-temperature properties with longer degassing times.

After heat treatment, the sample resistivity ratio was typically of the order of 500. In addition, thermal polishing had taken place, so that the sample now presented a bright, highly reflecting surface. Following the heating period, the current was abruptly shut off. The carbon resistor fell to

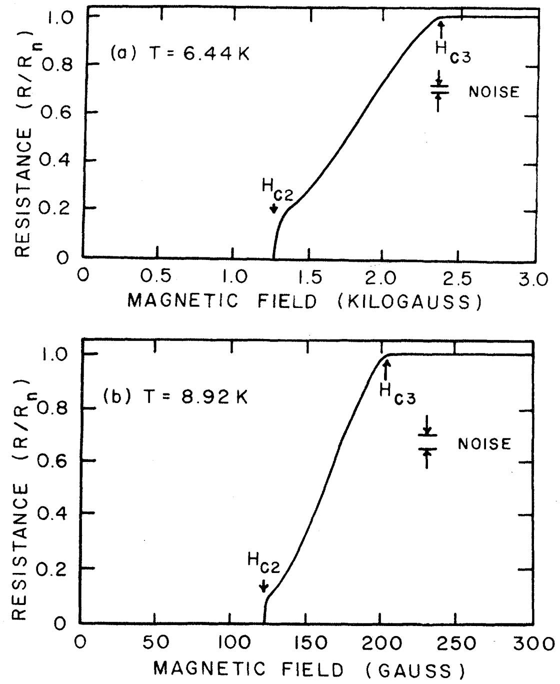

FIG. 2. (a) Resistive transition at $T = 6.44$ K. Measuring current was 25 mA. (b) Resistive transition at $T = 8.92$ K. Measuring current was 6.25 mA.

liquid-nitrogen temperature in about 15 min. The liquid nitrogen was then removed from the sample chamber and helium transferred. Total time from current shut-off until the sample passed through its critical temperature was about 1 h, with the pressure maintained at 1.6×10^{-9} Torr. Heat leakage into the sample chamber, primarily through the stainless-steel high-current lead, determined the minimum temperature attainable at 5.5 K. Temperature could be increased by passing regulated current through the resistance heater, and measured with the carbon resistor. The carbon resistor had been previously calibrated against a germanium standard resistor purchased from Scientific Instruments Inc.

Sample resistance as a function of applied field and temperature was measured by a standard four-terminal technique. A 6- to 25-mA measuring current was used at 370 Hz. Sample voltage was monitored with a phase-sensitive detector. Output from the detector was plotted on the y axis of a recorder, while the x axis was swept by the voltage across a standard resistor in series with the magnet current leads. By these means a complete set of resistance-versus-field curves were obtained for the cleaned sample. The sample chamber was then refilled with liquid nitrogen, the oxygen pressure in the chamber increased, and the sample reheated for 5 h. Upon cooling, a new set of resistance-versus-field curves were taken for comparison with the original set.

III. RESULTS AND DISCUSSION

A. Clean Samples

Figure 2 shows typical recorder tracings obtained on a degassed niobium sample. The ordinate, showing the phase detector output, is proportional to the sample resistance. The general curve shape was typical of all tracings taken on this and other samples subjected to the same preparatory treatment. Hysteresis was less than 1%. Curves taken in increasing fields were consistently used to determine the critical fields. The curves exhibit several distinct features which allow a determination of H_{c3} and H_{c2}. We observe a sharp onset of resistance at a field we identify as H_{c2}. At lower fields, superconductivity in the bulk effectively shorts the sample giving zero resistance. No evidence of flux-flow resistivity is observed between H_{c1} and H_{c2}, indicating that the flux lines are pinned and that the low current densities used were insufficient to overcome the pinning forces. At temperatures below 8.87 K, the measuring current was kept constant at 25 mA, for a calculated current density of 49 A/cm^2, assuming uniform distribution over the entire sample. At higher temperatures, the same current produced curves with a pronounced rounding of the H_{c2} transition. This we attribute to depinning of flux lines as the current density increases in the superconducting regions, leading to resistance below H_{c2}. Since this effect made it difficult to determine H_{c2}, we used a lower measuring current of 6.25 mA which produced sharpened transitions, as indicated in Fig. 2(b), near T_c. Though this resulted in an increased signal-to-noise ratio for these curves, we were largely able to average out the rapid noise fluctuations by using slow sweep times.

Above H_{c2}, the bulk of the sample is normal and superconductivity persists in a continuous sheath of thickness approximately $0.56\,\xi(t)$, where $\xi(t) = \xi_0/(1-t)^{1/2}$, and $\xi_0 = 387$ Å for pure niobium.[1] In this region, the resistance rises with field, as the sheath is in a resistive flux-flow state.[10] H_{c3} is identified as the field at which normal-state resistance returns.

A possible effect which could complicate the interpretation of these curves would be the persistance of superconductivity in regions of enhanced critical field, as might be the case near grain boundaries or other inhomogeneities. Such regions, if continuous along the length of the sample, would extend the field region in which zero resistance is observed, leading to H_{c2} values which are larger than expected for pure niobium. If discontinuous along the sample, these regions could lead to erroneous H_{c3} values by adding a high-field tail to the resistance curves. For a number of reasons

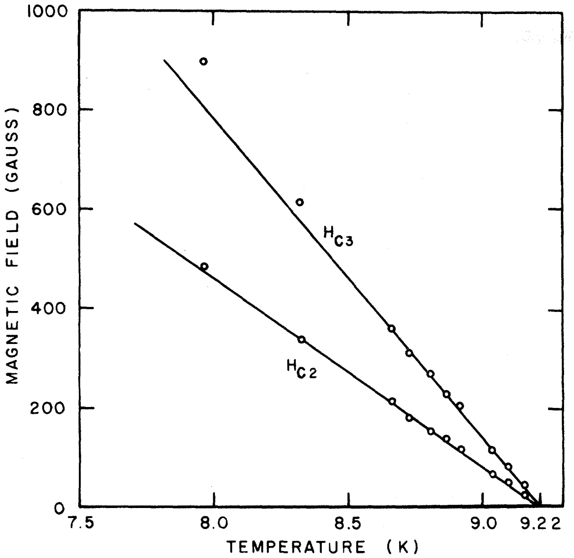

FIG. 3. H_{c3} and H_{c2} vs absolute temperature for degassed sample (1). Resistivity ratio is 470. Straight lines are best fits to points near T_c. Ratio of the two slopes gives $H_{c3}/H_{c2} = 1.71 \pm 0.05$.

we do not believe that this mechanism was present to a significant degree. For one, it is clear in Fig. 2 that no high-field tail was observed. Also, as discussed below, the measured temperature dependence of the ratio of surface to bulk critical fields agrees very well with theory. If the critical fields had been altered by inhomogeneities, we would to some extent expect the data to depart from ideal behavior. Similarly, from the measured temperature dependence of H_{c2}, we have calculated the Ginzburg-Landau parameter κ for our sample to be 0.76. This agrees well with other reported values for pure niobium,[1] and would indicate no significant anomalous behavior for our samples.

From a family of curves like those of Fig. 2 we have obtained Fig. 3. Here we plot H_{c2} and H_{c3} versus temperature, as recorded by the carbon thermometer in our sample holder. The thermometer could not be located closer than about 1 in. from the sample owing the very high temperatures reached in that region. Thus we expect a systematic error in the temperature determinations. In an attempt to determine this error, we mounted a second carbon thermometer near the sample in a preliminary run in which we did not heat the sample. This second thermometer read an average of 0.21 K higher then the original. Such an error, while not small, has little effect on the determinations of the ratio H_{c3}/H_{c2}. In much of the subsequent discussion, the critical fields are plotted against reduced temperature, where again the effect of such a systematic error is minimal.

We note that the H_{c3} curve shows a slight concavity with decreasing temperature. This behavior is consistent with the clean-limit theory of Ref. 4. Both curves approach a common T_c of 9.22 K, with the ratio of slopes near T_c calculated from the curves to be 1.71 ± 0.05, in good agreement with theory in that region. Thus, we observe none of the departures from theory which have been reported by others. This is emphasized in Fig. 4 where we have plotted H_{c3}/H_{c2} versus reduced temperature. For comparison, the Ginzburg-Landau (GL) and Hu-Korenman (HK) predictions are also indicated. The scatter of points near T_c reflects the error in taking the ratio of very small magnetic fields and the need to use a smaller measuring current near T_c. The data suggest a possible slight decrease below theory very near T_c. This decrease could be explained by a small sample misalignment in the field.

B. Samples heated in oxygen

The effects of introducing concentrations of oxygen into the previously cleaned samples are indicated in Figs. 5 and 6, in which H_{c2} and H_{c3} are plotted against reduced temperature for a clean sample (labeled *A*) and for two oxygen concentrations in this sample (labeled *B* and *C*). For each case, T_c was determined by extrapolating the corresponding curve of H_{c2} versus absolute temperature to $H_{c2} = 0$. The sample preparation conditions in each case are given in Table I. Treatment at lower oxygen pressures gave essentially no change in the measured values of H_{c2} and H_{c3}. This result was checked at oxygen pressure intervals up to 0.96×10^{-7} Torr. Thus the onset of the changes from clean behavior (*A*) occur in a rather narrow pressure range, between 0.96×10^{-7} and 2.5×10^{-7} Torr, and in this region the change in critical fields is quite large. The choice of the length of the heating interval was calculated as sufficient to reach equilibrium in the bulk.[9] However, it is also

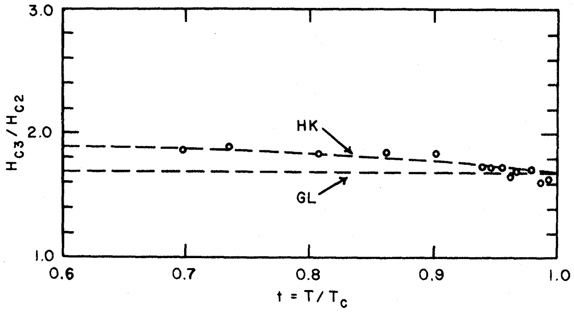

FIG. 4. H_{c3}/H_{c2} vs reduced temperature for sample (1). Dashed lines are theory of Hu and Koreman (HK), and the Ginzburg-Landau (GL) value 1.7.

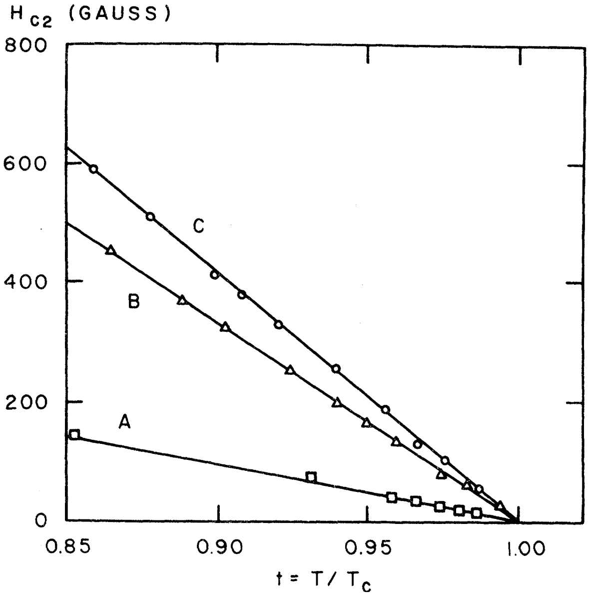

FIG. 5. H_{c2} vs reduced temperature for sample (2). Points A, B, and C taken after preparatory treatments given in Table I.

known that appreciable oxygen will migrate to the surface on cooling.[9,11] Recent measurements have indicated that the oxygen concentration is considerably enhanced in a layer approximately 30 Å in thickness near the surface.[11]

It is possible to calculate the bulk oxygen concentration in cases B and C by several methods. From the conditions of preparation given in Table I, we can determine the bulk concentration.[9] Also, DeSorbo[12] has presented the coefficient 5.2 $\mu\Omega$ cm/at.% for the change in bulk resistivity with oxygen concentration, and the value 0.93 K/at.% for the change in critical temperature. From the measured resistivities and critical temperatures we can thus determine the oxygen concentrations. The results of these calcualtions are presented in Table I. We note that the theoretical calculations and the experimental calculations based on the resistivity of the samples agree well with each other, but that the calculations based on the critical temperature suggest an oxygen concentration which is about an order of magnitude higher in each case. We will return to this point.

In Fig. 6 we have compared the H_{c3} data, near $t = 1$, with that expected from the expressions $H_{c3} = 1.7H_{c2}$. The agreement in the clean sample is excellent over the entire range, in accord with the results presented above, on a different sample. The agreement is also quite good up to about $t = 0.97$ for conditions B and C. At temperatures very close to $t = 1$ we find a pronounced enhancement of H_{c3} over the St. James–de Gennes value for both cases. The origin of this effect remains unclear. Oxygen residing in the surface would tend to cause a reduction in T_c there, as mentioned above, and if anything, would tend to depress H_{c3}. On the other hand, small amounts of carbide near the surface would lead to an enhanced T_c, and increase H_{c3} near $t = 1$. There is in fact some evidence that residual carbon migrates to the surface at elevated temperatures,[13] so it would seem worthwhile to pursue this point.

The possibility that residual oxygen at the surface might account for the type of behavior observed in Refs. 1 and 2 now seems less likely, since the most recent studies indicate the depth of such a layer to be about 30 Å.[11] Since this is considerably smaller than the coherence length in niobium, it is to be expected that the effect of such a layer would not significantly alter the boundary condition at the surface.

On the other hand, from Figs. 5 and 6, it is seen that reheating in oxygen does have a significant effect on the H_{c2} and H_{c3} data, in that the slope of both curves is considerably increased. This reflects an enhancement in the vlaues for the Ginzburg-Landau parameter κ, which we calculate for cases A, B, and C from our data, using the expression

$$\left.\frac{dH_{c2}}{dT}\right|_{T_c} = (2)^{1/2}\kappa\left.\frac{dH_c}{dT}\right|_{T_c} . \qquad (1)$$

For these calcualtions we have used $(dH_c/dT)_{T_c} = 415$ G/K.[1] The results are given Table I. The value $\kappa = 0.76$ for the cleaned sample is in excellent agreement with previously reported values

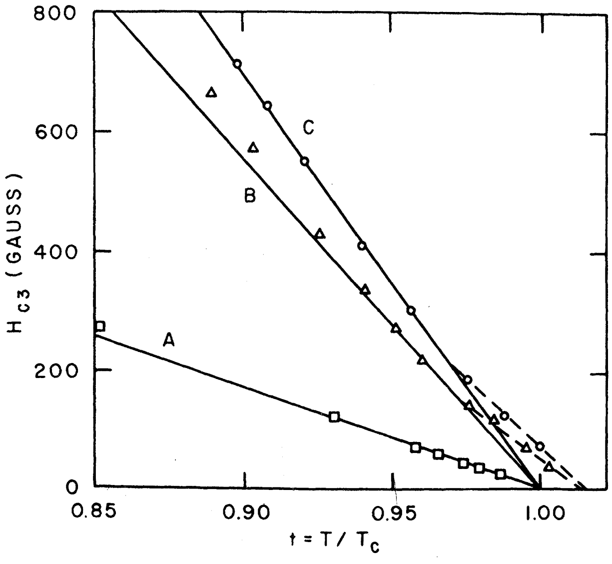

FIG. 6. H_{c3} vs reduced temperature for sample (2). Points A, B, and C taken after preparatory treatments given in Table I. Solid lines were determined from $H_{c3} = 1.7H_{c2}$. Dashed lines emphasize departures from theory near $t = 1.00$.

TABLE I. Conditions of preparation, resistivities, critical temperatures, oxygen concentrations, and κ values for sample (2).

Sample condition	Preparation conditions					Oxygen concentration (at. %) from			κ from	
	Temperature (K)	Pressure (Torr)	Time (h)	ρ ($\mu\Omega$ cm)	T_c (K)	preparation	ρ	T_c	Eq. (1)	Eq. (2)
A	2125 ± 50	1.6×10^{-9} (residual)	10	0.027	9.34	< 0.001			0.76	0.76
B	2125 ± 50	2.5×10^{-7} (oxygen)	5	0.051	9.30	0.008	0.005	0.040	2.47	0.79
C	2125 ± 50	5.0×10^{-7} (oxygen)	5	0.100	9.22	0.015	0.014	0.12	3.04	0.82

for pure niobium.[1] However, the values obtained for cases *B* and *C* are considerably larger than those expected from the measured bulk resistivity, using the expression[14]

$$\kappa = \kappa_0 + 7.5\times10^3\gamma^{1/2}\rho \ . \qquad (2)$$

Here, $\kappa_0 = 0.76$ and the coefficient of the electronic specific heat $\gamma = 6933$ erg/cm^{3}K^2. The resistivity ρ is measured in Ω cm. These calculations are also presented in Table I. The measured κ values suggest an increase in resistivity of the order of 100 times that actually measured for the bulk.

The fact that the measured κ values are larger than expected from the bulk resistivity, and that, as mentioned above, the observed reduction in critical temperature is also larger than expected, has led us to conclude that our H_{c2} and H_{c3} curves for *B* and *C* are not characteristic of the bulk of our sample. This is because both T_c and κ are determined from the H_{c2} curve. Instead, we believe our measured critical fields are the "bulk" and surface critical fields of a surface layer of much reduced mean free path, which has formed during the reheating. Such a layer would have to be considerably thicker than 30 Å in order to affect H_{c2} and H_{c3} to the extent observed. Hence, a possible surface layer of enhanced oxygen concentration would not seem to be the primary cause. Instead, it is more likely that a much larger layer of greatly increased roughness has formed. Varmazis *et al.*[11] have shown that the surface of niobium heated in oxygen takes on a rough, faceted structure to a depth of several microns. We believe that our measurements reflect the formation of this layer. Since our sample has a thickness of 50 μm, it is quite reasonable that such a layer could exist yet not be reflected in measurements of the bulk resistivity. On the other hand, such a layer could carry the transport current until its critical field was reached, leading to H_{c2} and H_{c3} values characteristic of it and not the bulk of the sample.

IV. CONCLUSIONS

We have found that resistive measurements of H_{c3}/H_{c2} in thoroughly degassed pure niobium agree well with clean-limit theory, a result unchanged by reheating in oxygen atmospheres of up to 0.96×10^{-7} Torr. We have not observed the decrease in this ratio near T_c reported by others. The samples in Refs. 1 and 2 appear to have been prepared quite carefully, and we would expect had a surface quality comparable to ours. Thus, it might be worthwhile to explore the differences between susceptibility and resistive measurements of the critical fields, possibly by carrying both out on the same samples.

We have also observed a considerable increase in H_{c2} and H_{c3} in samples reheated at above 0.96×10^{-7} Torr oxygen pressure. Nonetheless, the ratio of critical fields remains 1.7 to temperatures quite near T_c. The increased κ values and decreased critical temperatures which are measured for these samples strongly suggest that a surface layer of increased resistivity over the bulk has formed under this treatment. We attribute the formation of such a layer largely to the onset of diffuse surface scattering due to the formation of a faceted structure at the surface. A residual enhancement of H_{c3} above the Ginzburg-Landau value very near T_c in these samples has yet to be understood, although we have suggested the presence of carbides at the surface as an explanation.

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